DETERMINATION OF OPTICAL CONSTANTS OF MATERIALS USING BEER-LAMBERT LAW

PROJECT REPORT

Submitted by

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ST.TERESA'S COLLEGE (AUTONOMOUS), ERNAKULAM

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ST.TERESA'S COLLEGE (AUTONOMOUS),

ERNAKULAM

CERTIFICATE

This is to certify that the project report titled **"DETERMINATION OF OPTICAL CONSTANTS OF MATERIALS USING BEER-LAMBERT LAW "** submitted by ANNA ANTONY towards partial fulfillment of the requirements for the award of degree of bachelor of physics is a record of bonafide work carried out by them during the academic year 2022-2023.

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PROJECT REPORT

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Year of Work: 2022-2023

This is to certify that this project work entitled **"DETERMINATION OF OPTICAL CONSTANTS OF MATERIALS USING BEER-LAMBERT LAW "** is an authentic work done by ANNA ANTONY.

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Date: 25/04/2023

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DECLARATION

I, ANNA ANTONY final year BSc. Physics student, Department of Physics St. Teresa's College, Ernakulam do hereby declare that the project work entitled " **DETERMINATION OF OPTICAL CONSTANTS OF MATERIAS USING BEER-LAMBERT LAW** " has been originally carried out under the guidance and supervision of Smt. MINU PIUS, Assistant Professor, Department of Physics, St. Teresa's College (Autonomous), Ernakulam in partial fulfilment for the award of the degree of Bachelor of Physics. We further declare that this project is not partially or wholly submitted for any other purpose and the data included in the project is collected from various sources and are true to the best of our knowledge.

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PLACE: ERNAKULAM

DATE: 19/04/2023

DETERMINATION OF OPTICAL CONSTANTS OF MATERIALS USING BEER-LAMBERT LAW

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ABSTRACT

In this project, we investigated the absorption spectra of different materials for the verification of Beer Lambert law and its application in analyzing the linear fit of absorbance versus concentration of given samples. The optical constants of zinc ferrite were estimated, and the photo catalytic degradation of dyes was also studied. Beer-Lambert Law states that the concentration of a solution for a known path length is directly proportional to its absorption of light.

CONTENTS

CHAPTER I

INTRODUCTION

BEER LAMBERT LAW

I_0 is the intensity of light entering a solution and I_t is the intensity of light exiting the solution, then the transmittance, T, of the solution is given as I_1/Io. Transmittance is also expressed as a percentage, $(I_t/Io)(100\%)$. Frequently, the absorbance, A, rather than transmittance is used for the amount of light a solution absorbs. Absorbance is defined by the equation: $A = -\log(T)$ or $A = \log(Io/It)$.

The absorbance of a solution depends on the quantity of light absorbed by the species in the solution, the wavelength of the light entering the solution,the length of the solution the light has to pass through, and the concentration of the solution.This relationship is known as Beer's law and is expressed mathematically as

$$A = \varepsilon cl,$$

where 'A' is the absorbance of the substance, 'ε' is the molar absorptive, 'l' is the length of the light path, and 'c' is the concentration of the substance.

In this experiment an absorption spectra curve of absorption versus wavelength will be obtained for all the materials. From the absorption spectra, the wavelength of maximum absorption is determined and a calibration curve relating absorption to concentration for materials is also obtained and optical constants were also determined. From the Beer-Lambert relation,the analysis of coefficient value of absorbance A gives us the information about direct band gap and indirect band gap. Photo catalytic degradation of the two dyes were also studied considering the reduction in concentration level due to the exposure to sunlight.

A) OPTICAL CONSTANTS

The optical constants of a material are numbers which describe the manner in which a plane electromagnetic wave progresses through the material. The constants, a pair for every frequency, measure the speed and the attenuation of the wave. These constants have value not only for describing the wave progress but also for their intimate relation to the fundamental constitution of the material. The frequency dependence of the optical constants gives a large amount of information about the physical nature of the material. Because of the electric nature of the particles which make up the material, the electromagnetic wave is a natural handle with which to shake the material and thereby learn about its constitution; to find its resonance frequencies; to test its uniformity; etc.

1. Refractive index

Refractive index is a material property that describes how the material affects the speed of light travelling through it.Refractive Index (Index of Refraction) is a value calculated from the ratio of the speed of light in a vacuum to that in a second medium of greater density. The refractive index is usually represented by the symbol n or μ. A wave front incident upon a plane surface separating two media is refracted upon entering the second medium if the incident wave is oblique to the surface. The refractive index or index of refraction is the ratio between the velocity of light c in free space (for all practical purposes, either air or a vacuum) and its velocity (v) in a particular medium: $n = c/v$

The refractive index of a medium is dependent upon the frequency of light passing through, highest frequencies having the highest values of n. In this project we find the refractive index of zinc ferrite nanoparticle, methylene blue and methyl orange from beer lambert law using spectrophotometer. Spectrophotometer is an instrument that measures the amount of intensity of light absorbed by the sample solution as a function of wavelength. This technique of measuring the amount of absorbed light through sample solution is known as spectrophotometry.Here we used empirical equations to find refractive index of the samples:

According to equation of Ravindra,

$$\text{Refractive index, } n = \alpha + \beta E_g$$

where, $\alpha = 4.048\ eV^{-1}$ and $\beta = -0.62\ eV^{-1}$

According to equation of Vandamme

$$\text{Refractive index, } n = \sqrt{1 + \left(\frac{A}{Eg+B}\right)^2}$$

where, A = 13.6 eV and B = 3.4 eV

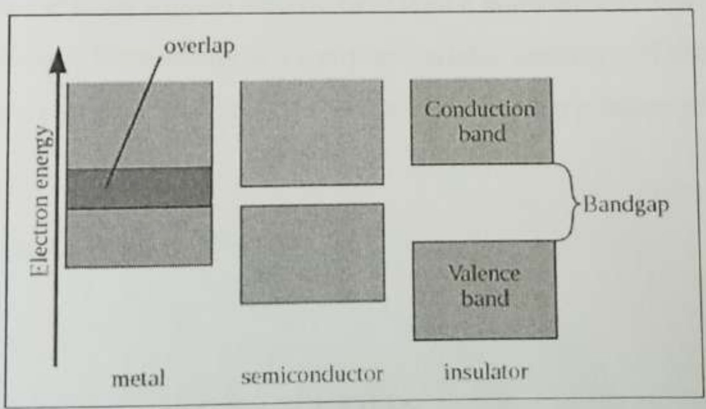
2. Extinction Coefficient (k)

Extinction coefficient k represent the imaginary part of the refractive index and is a function of the absorption coefficient and wavelength. It tells how strongly a sample absorbs or reflects radiation or light at a particular wavelength.

$$\text{Extinction Coefficient, } k = \frac{A\lambda}{4\pi}$$

3. Band gap

In solid-state physics, a band gap, also called a band gap or energy gap, is an energy range in a solid where no electronic states exist. In graphs of the electronic band structure of solids, the band gap refers to the energy difference (often expressed in electron volts) between the top of the valence band and the bottom of the conduction band in insulators and semiconductors. It is the energy required to promote an electron from the valence band to the conduction band. The resulting conduction-band electron (and the electron hole in the valence band) are free to move within the crystal lattice and serve as charge carriers to conduct electric current.



There are two types of band gap energy namely direct and indirect gap.

The key difference between direct and indirect band gap is that in direct band gap, the crystal momentum of electrons and holes remains the same in the conduction band and the valence band and an electron can directly emit a photon, whereas indirect band gap has different k-vectors where a photon cannot be emitted.

Band gap can be found out using the equation $h\nu(eV) = \frac{hc}{\lambda} = \frac{1242}{A}$ where A is absorption value, h = $6.62607015 \times 10^{-34}$ m2 kg / s . planck's constant . λ = wavelength

The band gap in the absorption spectrum corresponds to the point at which absorption begins to increase from the baseline, since this indicates the minimum amount of energy required for a photon to excite an electron across the band gap and thus be absorbed in the semiconductor material.

A detailed band gap analysis involves plotting and fitting the absorption data to the expected trend lines for direct and indirect band gap semiconductors. The equation is:

$\alpha h\nu \propto (h\nu - Eg)^n$ when n=1/2 we will get the value of direct band gap whereas n=2 gives indirect band gap.

4. Permittivity

In electromagnetism, the absolute permittivity, often simply called permittivity and denoted by the Greek letter ε (epsilon), is a measure of the electric polarizability of a dielectric. A material with high permittivity polarizes more in response to an applied electric field than a material with low permittivity, thereby storing more energy in the material. Permittivity is a complex variable consisted of the real part (dielectric constant) and imaginary part (dielectric loss). The real and imaginary values of permittivity are related to the constant n and k.

$$\text{Permittivity, } \varepsilon^* = \varepsilon' + i\,\varepsilon''$$

B) PHOTOCATALYTIC DEGRADATION

Photocatalysis is a process in which light energy is used to drive pairs of chemical reactions. Through the absorption of light, an excited electron/ hole pair is produced. The principle of heterogeneous photocatalysis is based on the promotion of electrons from valence band to the conduction band through the illumination of a semiconductor with photons of energy equal to or greater than its gap energy. A highly efficient degradation produces carbon dioxide and water as the end products.

CHAPTER II

A) PRINCIPLE

Beer- Lambert's Law

The Beer-Lambert law is a linear relationship between the absorbance (A) and the concentration (c), molar absorption coefficient (ε) and optical path length (l) of a solution:

$$A=\varepsilon cl$$

We create an absorbance versus wavelength graph using the absorbance values of various solution concentrations for a range of wavelengths (200nm to 800m). Finally, create a graph of absorbance vs concentration using the absorbance value to determine the transmittance %, from which the refractive index is determined. The Beer-Lambert law relates the attenuation of light to the properties of the material through which the light is traveling. The Absorbance of a Solution:-For each wavelength of light passing through the spectrometer, the intensity of the light passing through the blank (reference) is measured. This is usually referred to as Io. The intensity of the light passing through the sample is also measured for that wavelength which is denoted by I. If I is less than Io, then the sample has absorbed some of the light (neglecting reflection of light off the cuvette surface). A simple bit of math is then done in the computer to convert this into something called the absorbance of the sample - given the symbol, A. The absorbance of a transition depends on two external assumptions.

1. The absorbance is directly proportional to the concentration (c) of the solution of the sample used in the experiment.
2. The absorbance is directly proportional to the length of the light path (l), which is equal to the width of the cuvette.

Assumption 1: Absorbance to concentration can be expressed as $A \propto c$

The absorbance (A) is defined via the incident intensity Io and transmitted intensity I by

$$A = log_{10}\left(\frac{I_o}{I}\right)$$

Assumption 2: Absorbance to length can be expressed as $A \propto l$

This proportionality can be converted into an equality by including a proportionality constant (ϵ).

$$A=\epsilon cl$$

This is Beer-Lambert's Law.

$$A = log_{10}\left(\frac{I_o}{I}\right) = \epsilon cl$$

The refractive index, n, of a material is defined as

$$n= c/v$$

Where c is the speed of light in a vacuum and v the speed of light in the material.

B) MATERIALS REQUIRED

1. Spectrophotometer

A **spectrophotometer** is a device that is used to measure the amount of light absorbed by a sample at different wavelengths. A spectrophotometer measures the amount of light that can pass through a sample. It consists of a light source, a sample holder, a diffraction grating or prism to separate the light into its different wavelengths, and a detector to measure the amount of light absorbed at each wavelength. Spectrophotometry is a standard technique in many chemistry labs. From the data collected, a computer plots an absorbance spectrum for the sample. Spectrophotometry is the action of using a spectrometer to take a measurement. In simple terms, a spectrophotometer is a tool that helps scientists and researchers study the properties of light and how it interacts with different materials. By measuring the amount of light absorbed by a sample at different wavelengths, a spectrophotometer can provide valuable information about the composition and properties of the sample. A spectrophotometer can be a useful tool for conducting experiments and studying the properties of light and matter. For example, a student could use a spectrophotometer to study the absorption spectrum of a solution, which is the pattern of light absorption at different wavelengths. By analyzing the absorption spectrum of a solution, a student can learn about the composition and properties of the solution. The basic idea of spectrophotometry is that light passes through a sample and the intensity of the beam is compared before and after the sample. Different samples will absorb light differently and allow different amounts to pass-through of different colors of light.

2. **Zinc ferrite**

Zinc ferrites are a series of synthetic inorganic compounds of zinc and iron (ferrite) with the general formula of ZnxFe$_3$−xO4. Zinc ferrite compounds can be prepared by aging solutions of $Zn(NO_3)_2$, Fe(NO$_{3)3}$, and triethanolamine in the presence and in the absence of hydrazine,[1] or reacting iron oxides and zinc oxide at high temperature.

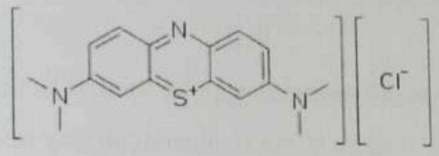
Zinc ferrite ($ZnFe_2O_4$) has been studied extensively due to its high electromagnetic performance, excellent chemical stability, mechanical hardness, low coercively, and moderate saturation magnetization, which make it a good contender for applications as soft magnets and low-loss materials at high frequencies

3. **Methylene blue** ($C_{16}H_{18}ClN_3S$)

Methylene blue is a colorful organic chloride salt compound used in medicine and by biologists as a dye to help them see under the microscope. It is also known as Methylthioninium chloride or Swiss blue. It is represented by the formula

$$C_{16}H_{18}ClN_3S$$

Methylene blue is a thiazine dye. It also acts as an oxidation-reduction agent. A compound consisting of dark green crystals or crystalline powder, having a bronze-like luster. Solutions in water or alcohol have a deep blue color. Methylene blue is used as a bacteriologic stain and as an indicator.



Formula of methylene blue

Methylene blue is represented by the formula $C_{16}H_{18}ClN_3S$

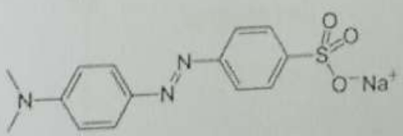
It has 3,7-bis(dimethylamino) phenothiazine - 5 - ium as the counterion. Its IUPAC name is

7-(dimethylamino)phenothiazin−3−ylidene

7-(dimethylamino)phenothiazin−3−ylidene - methyl azanium; chloride.

4. **Methyl Orange**

Methyl orange is a pH indicator frequently used in titration because of its clear and distinct color variance at different pH values. Methyl orange shows red color in acidic medium and yellow color in basic medium.



In a solution that decreases in acidity, methyl orange moves from the color red to orange and finally to yellow with the opposite occurring for a solution increasing in acidity.

C) EXPERIMENTAL SETUP

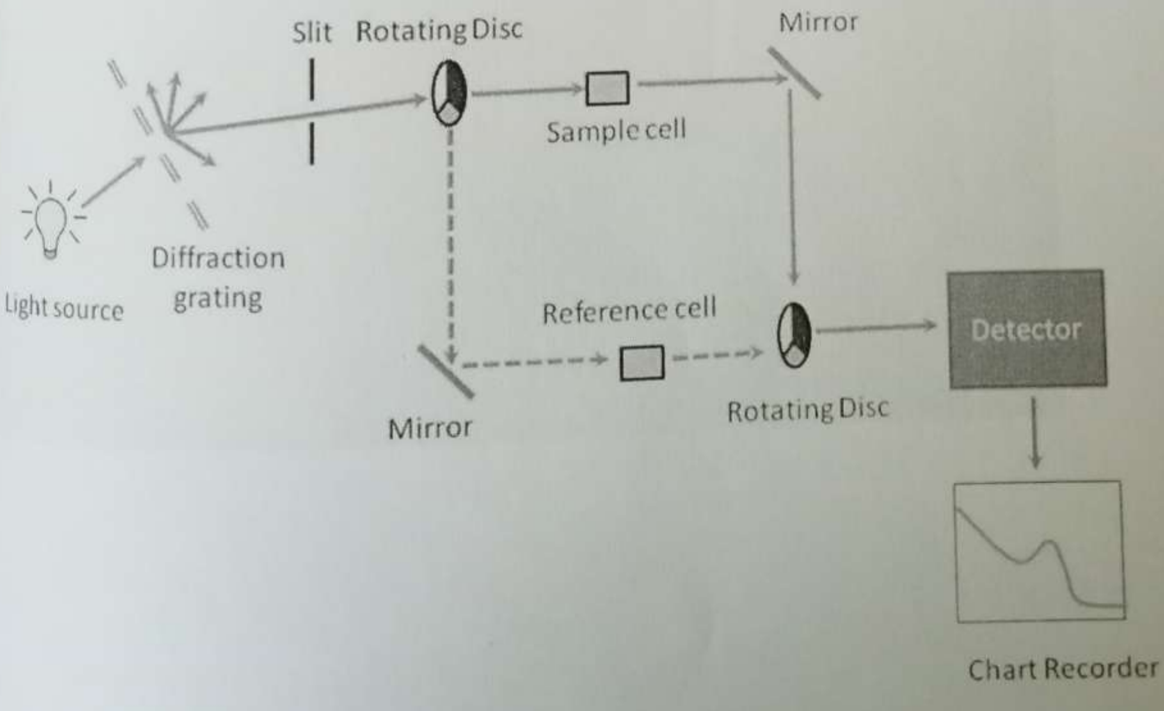
Spectrophotometer works on the principle of Beer- Lambert's law. Detection of functional groups, identification of unknown compounds, detection of impurities are some the application. It has the following basic components.

Source – A continuous source of radiant energy covering the region of spectrum in which the instrument is designed to work . UV - Hydrogen deuterium lamp ,Visible – Tungsten lamp

Filters and monochromators - A light filter is a device that allow light of the required wavelength to pass but absorbs light of the other wavelength wholly or partially. Filters are of two types :-Absorption filter & Interference filters. Monochromators – The monochromators is to disperse the radiation according to the wavelength .

Cell / sample holder – The cell holding the sample (usually a solution should be transparent to the wavelength region being recorded.

Detector – In order to detect radiation, three types of photosensitive devices are: Photovoltaic cell, Phototube, Photomultiplier.



The light source produces the photons that will pass through the sample. The exact type of light source will depend on the wavelength of light needed. Depending on the source, a collimator and prism select the correct wavelength. The light interacts with the sample next. A quartz cuvette holds the samples. A cuvette is a specialized piece of glassware with a very precise width and material. The material of the sample holder is important. You don't want to use a sample holder that will also absorb at the wavelength of light you are investigating. This is also why it is best practice to run a blank/background in the instrument with an empty cuvette. The path length through the cuvette is also an important parameter for some calculations. The path length is the amount of sample the light passes through. So a cuvette that is 1 cm wide has a path length of 1 cm. After the light passing through the sample, it travels to the detector. Similar to the light source, the exact detector will depend on the wavelength of light. Some of the most common detectors are photomultiplier tubes and photodiodes. The detector counts the number of photons reaching it. The detector connects to a computer that plots this data. This plot is called an absorption spectrum. It is a plot of light intensity verse the wavelength of light.

D) Preparation of samples

Preparation of Dyes (methylene blue and methyl orange)

We have 100 ppm of dye prepared as the stock with distilled water as the base fluid.

By using the equation,

$$M_1V_1=M_2V_2$$

$$100ppm * V_1=10ppm * 2ml$$

$$V_1=\frac{10ppm*2ml}{100ppm}=0.2ml=200\mu l$$

To make 2 ml of dye with 10 ppm concentration, we are taking 200 µl of dye from the already concentrated solution of 100 ppm by adding 2 ml of water to it. Distilled water is taken as the blank as water is the base fluid for the prepared solution . When placing a cuvette into the Spectrophotometer, the clear side should be facing towards the front to allow light source to pass through it. The solution has been tested on and the data have been collected from the software.

CHAPTER III

OBSERVATIONS AND GRAPHS

Readings have been taken and graph is plotted using Origin Pro Software

A) ABSORPTION SPECTRUM

A1. Absorption spectrum of zinc ferrite

Peak wavelength = 280nm

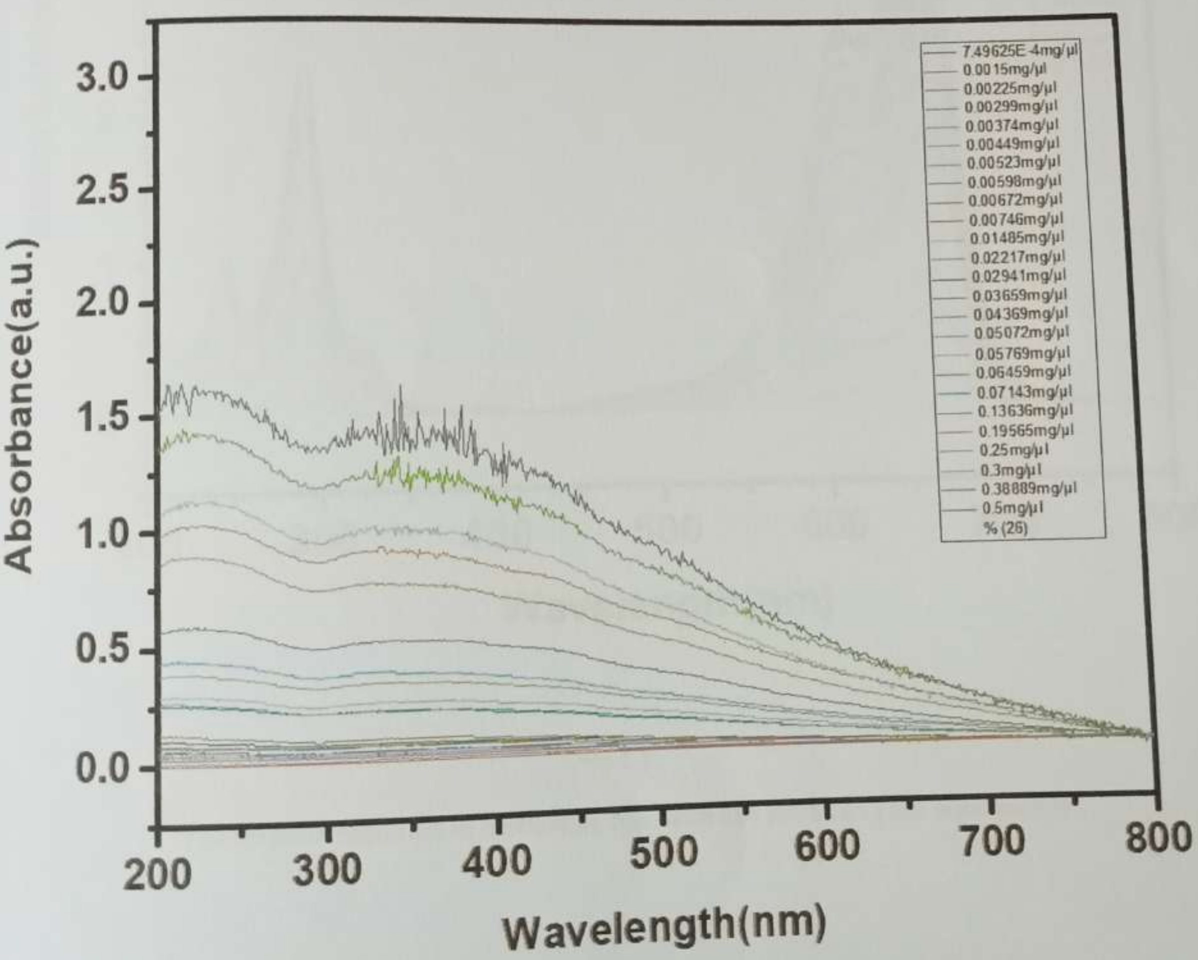


fig. 1.0

(Absorption spectrum of zinc ferrite nanoparticle with 280 nm wavelength as its peak)

Concentration equation: 1ml

$$\frac{1*10^{-6}}{(2000+1)*10^{-6}} * 1.5\ mg/\mu l = 7.496252*10^{-4}\ mg/\mu l$$

A2. Absorption spectrum of methylene blue

Peak wavelength = 664nm

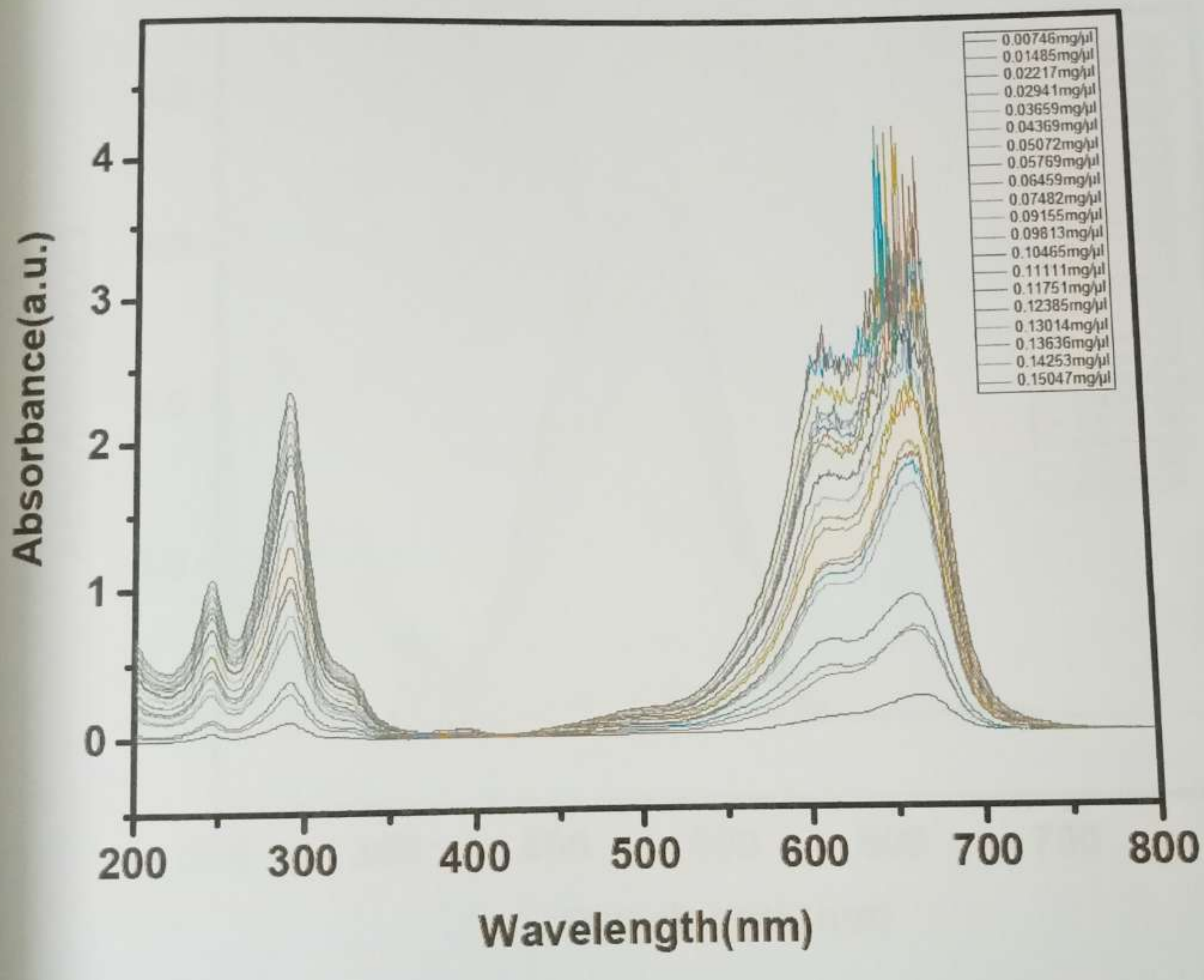


fig.1.1

(Absorption spectrum of methylene blue with 664 nm as its peak wavelength)

A3. Absorption spectrum of methyl orange

Peak wavelength = 465nm

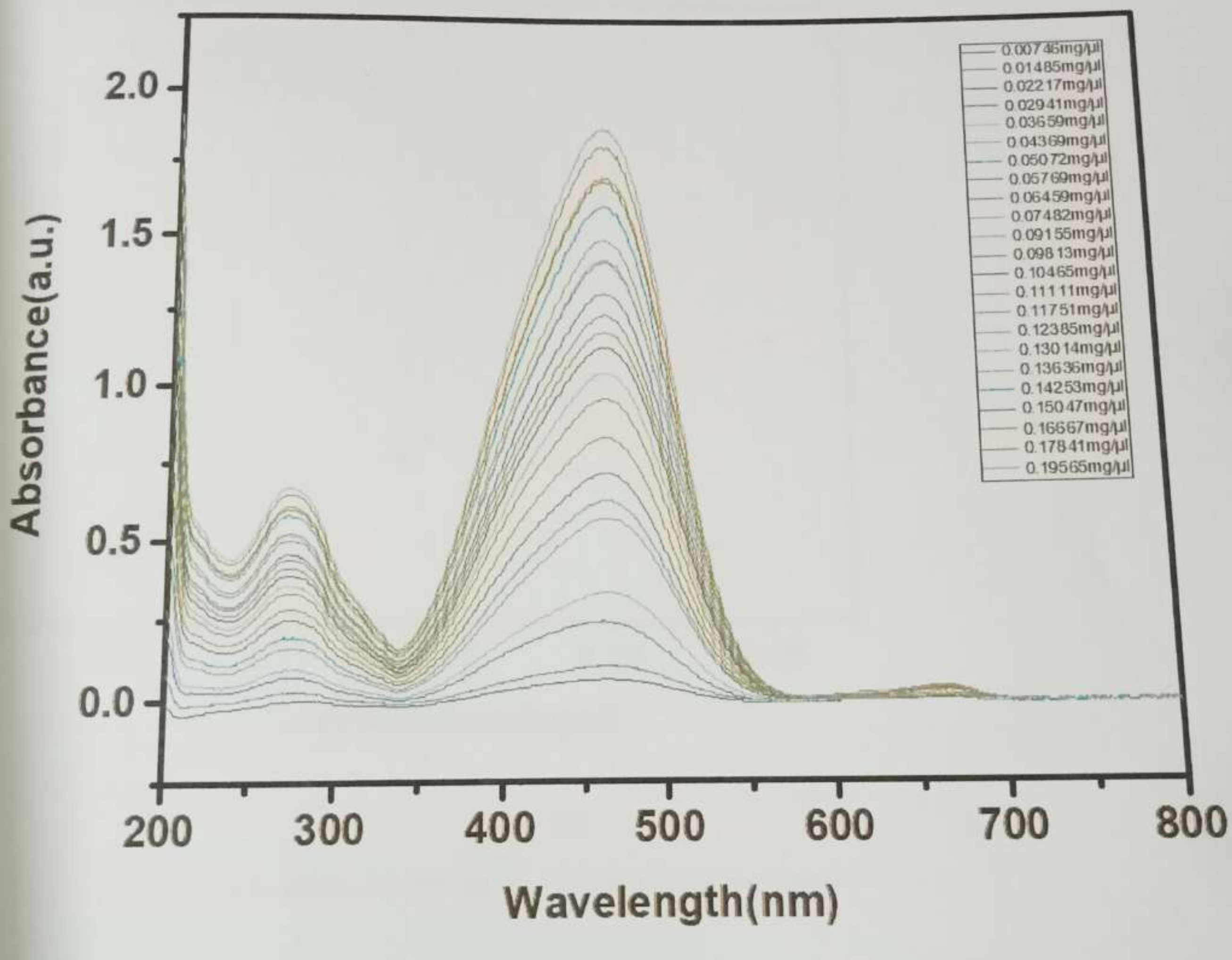


fig.1.2

(Absorption spectrum of methyl orange with 465 nm as its peak.)

B) LINEAR FIT FOR ABSORBANCE VERSUS CONCENTRATION

B1. Linear fit for absorbance versus concentration of zinc ferrite

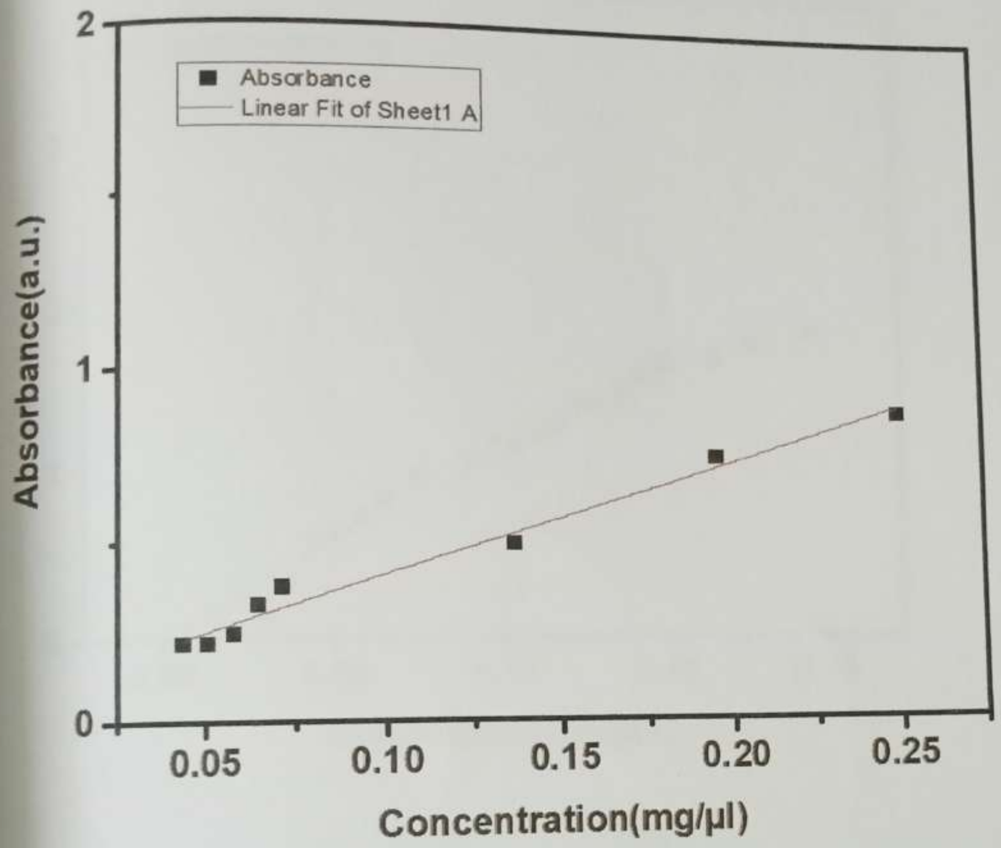


fig. 2.0

(linear fitting between absorbance vs. concentration of zinc ferrite)

Equation	y = a + b*x
Plot	A
Weight	No Weighting
Intercept	0.08585 ± 0.02425
Slope	3.26529 ± 0.18567
Residual Sum of Squares	0.00865
Pearson's r	0.99044
R-Square (COD)	0.98097
Adj. R-Square	0.9778

B2. Linear fit for absorbance versus concentration of methylene blue

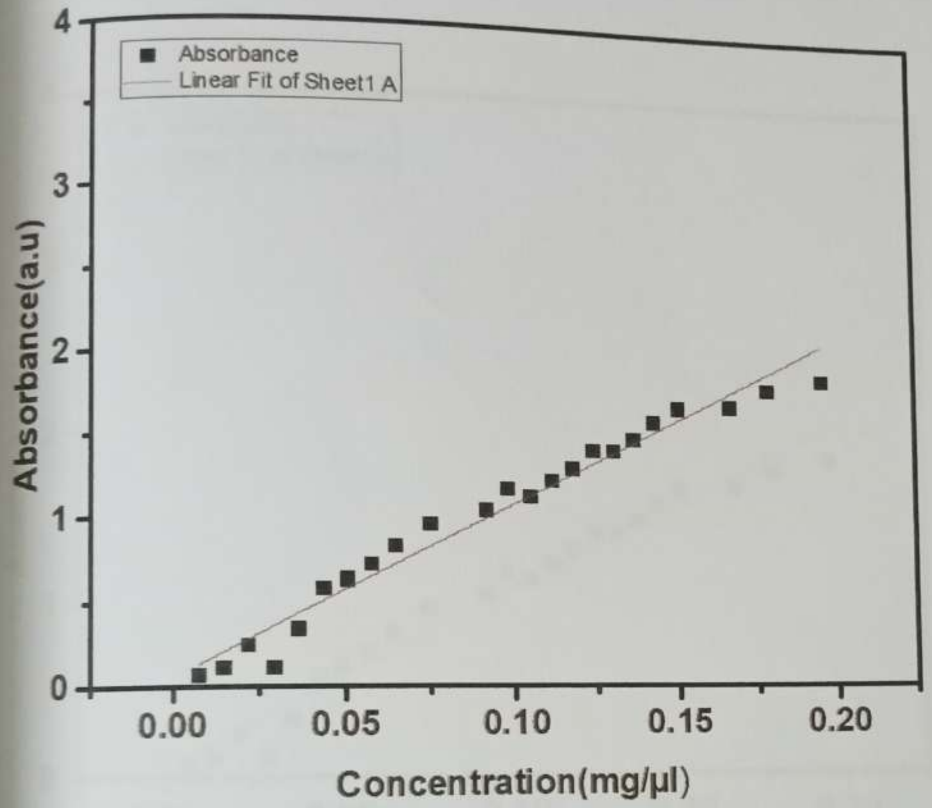


fig.2.1

(linear fitting between absorbance vs. concentration of methylene blue)

Equation	y = a + b*x
Plot	A
Weight	No Weighting
Intercept	0.52842 ± 0.20006
Slope	22.12339 ± 2.37004
Residual Sum of Squares	2.80797
Pearson's r	0.91916
R-Square (COD)	0.84486
Adj. R-Square	0.83517

B3. Linear fit for absorbance versus concentration of methyl orange

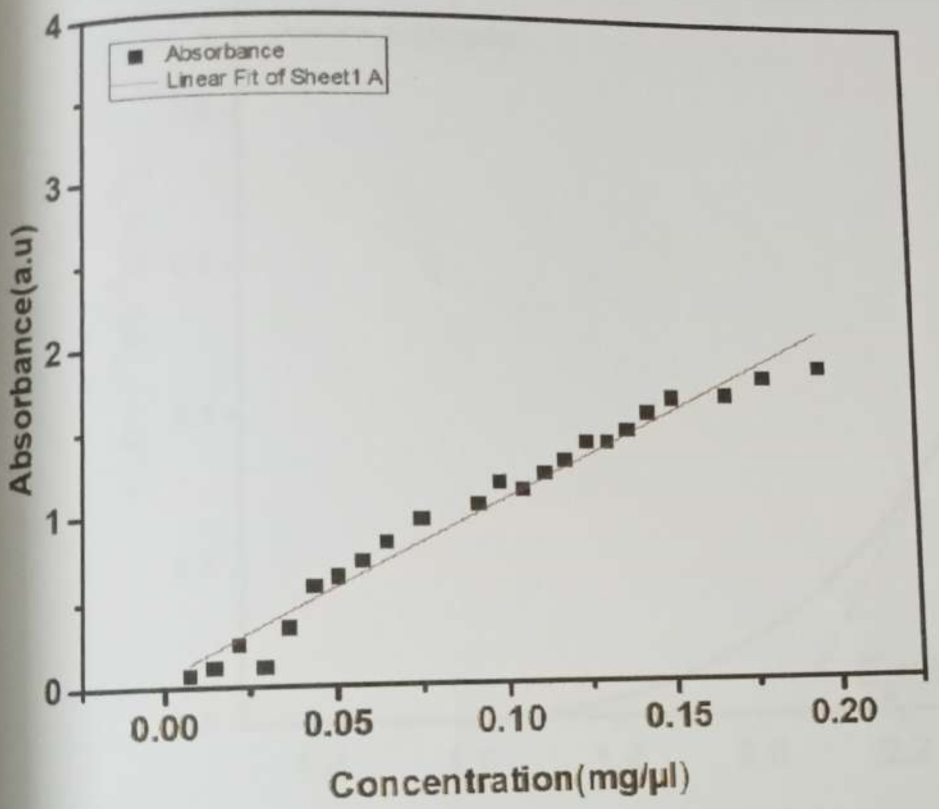


fig.2.2

(linear fitting between absorbance vs. concentration of methyl orange)

Equation	y = a + b*x
Plot	A
Weight	No Weighting
Intercept	0.04874 ± 0.04335
Slope	10.39666 ± 0.40209
Residual Sum of Squares	0.22607
Pearson's r	0.98466
R-Square (COD)	0.96955
Adj. R-Square	0.9681

C) BAND GAP OF ZINC FERRITE

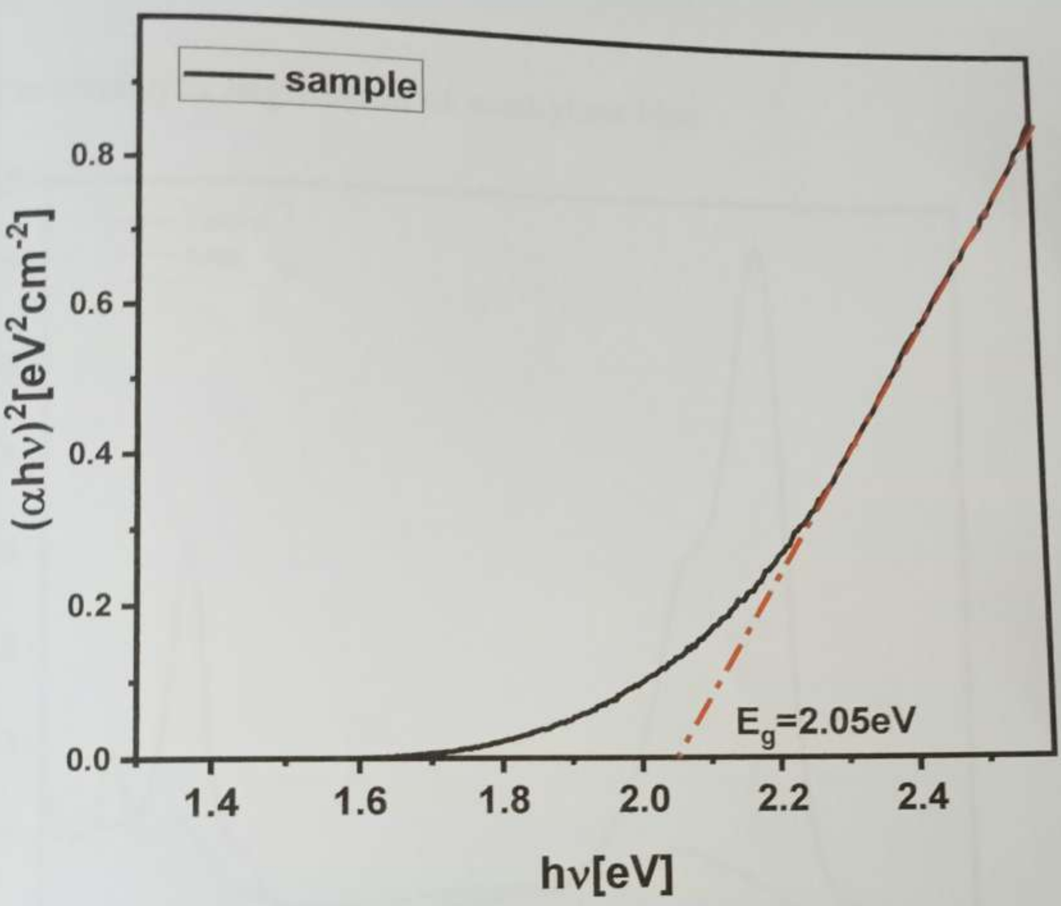


fig.3.0

(direct energy band gap of zinc ferrite)

The conversion between wavelength (nm) and band gap energy (eV) units is achieved by

$hv(eV) = \frac{hc}{\lambda} = \frac{1242}{A}$ where A is absorption value, h = 6.62607015 × 10-34 m2 kg / s , planck's constant , λ = wavelength

$Ahv \propto (hv - Eg)^n$ when n=1/2 we will get the value of direct band gap whereas n=2 gives indirect band gap.

Therefore the direct bad gap energy, $E_g = 2.05eV$

D) PHOTOCATALYTIC DEGRADATION OF DYES

Photocatalytic degradation was studied for the two dyes under the exposure of sunlight .

D1. Photocatalytic degradation of methylene blue

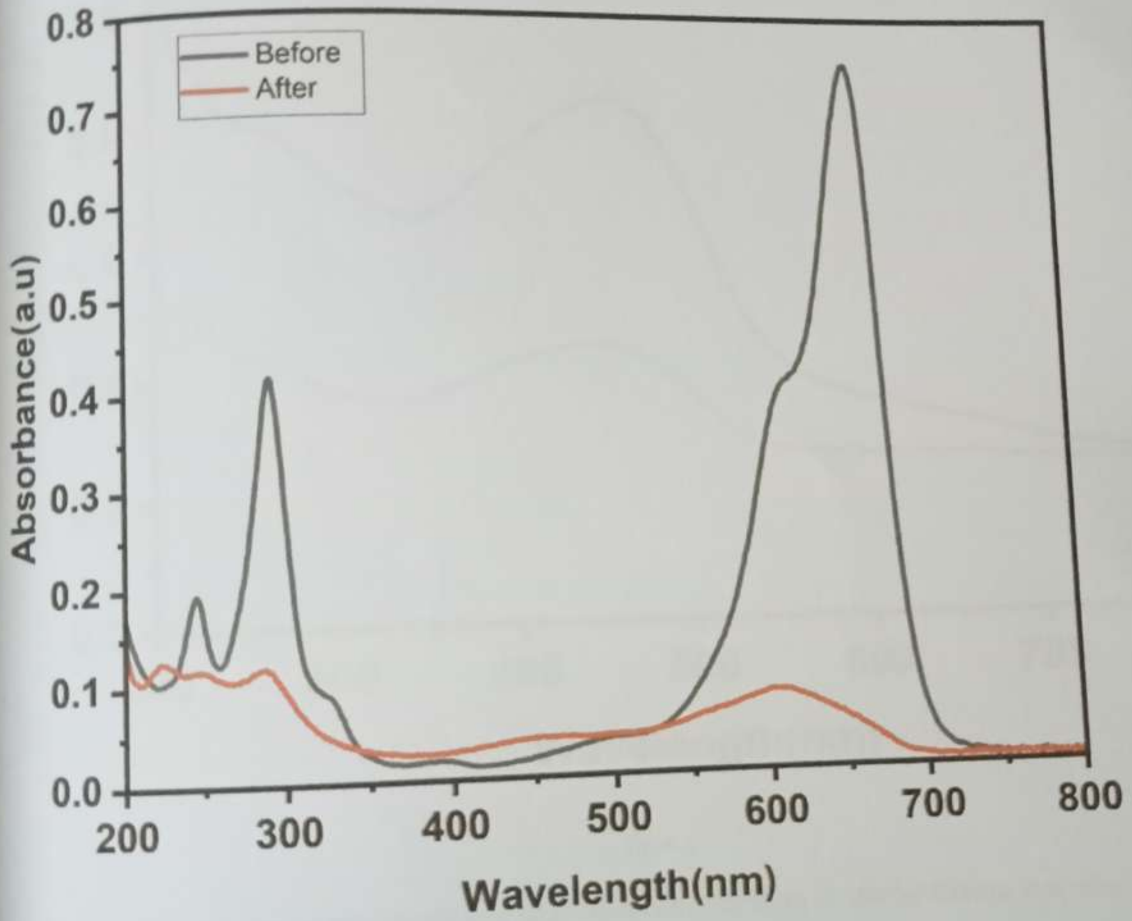


fig.4.0

{the graph shows the before(black) and after (red) concentration of Methylene blue dye when undergone photocatalytic degradation}

Methylene blue		
Equation:	y = a + b*x	
Intercept, a	0.52842	
Slope, b	22.12339	
	Before	After
Absorbance	0.75062	0.12681
Concentration	0.010043	-0.018153

D2. Photocatalytic degradation of methyl orange

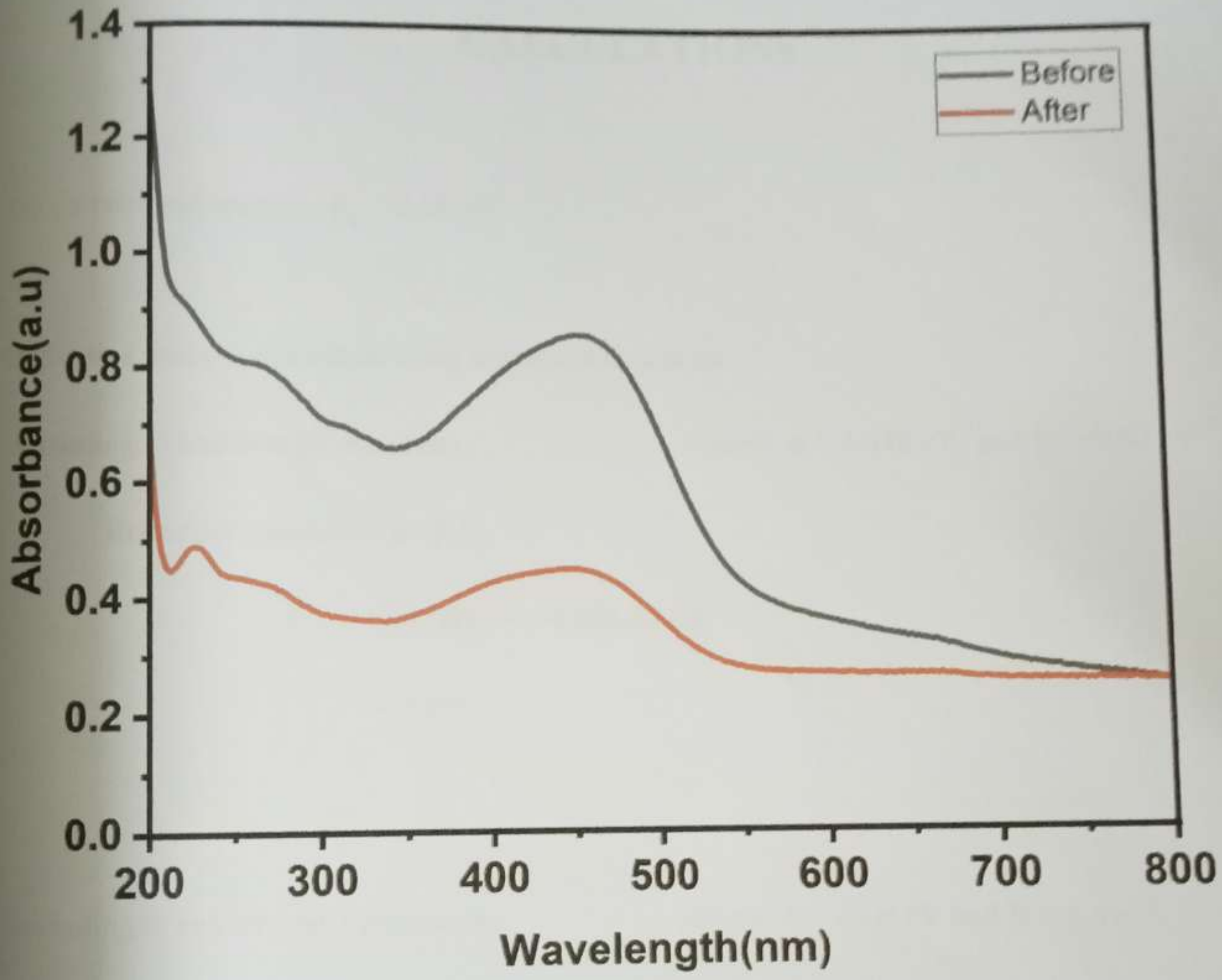


fig.4.1

{the graph shows the before(black) and after (red) concentration of Methyl Orange dye when undergone photocatalytic degradation}

Methyl Orange		
Equation:	y = a + b*x	
Intercept, a	0.04874	
Slope, b	10.39666	
	Before	After
Absorbance	0.85806	0.45145
Concentration	0.07784	0.038734

CHAPTER IV

CALCULATIONS

Direct band gap energy , $E_g = 2.05$ eV

Refractive index is calculated using empirical equations

According to equation of Ravindra, where, $\alpha = 4.048\ eV^{-1}$ and $\beta = -0.62\ eV^{-1}$

Refractive index, $n = \alpha + \beta E_g$

$= (4.048) + (-0.62)*(2.05)$

$= 2.777$

According to equation of Vandamme, where, A = 13.6 eV and B = 3.4 eV

Refractive index, $n = \sqrt{1 + \left(\frac{A}{Eg+B}\right)^2}$

$= \sqrt{1 + \left(\frac{13.6}{2.05 + 3.4}\right)^2}$

$= 2.688$

Mean **Refractive Index**, $n = \frac{2.777+2.688}{2} = 2.7325$

https://iopscience.iop.org/article/10.1088/1757-899X/515/1/012047

Absorption edge, $\lambda = \frac{1242}{Eg} = \frac{1242}{2.05} = 605.85nm$

A=0.18004 (value of A for λ = 605nm from readings)

Extinction Coefficient, $K = \frac{A\lambda}{4\pi} = \frac{0.18004 * 6.0585 * 10^{-9}}{4\pi} = 8.6801 * 10^{-9}$

Permittivity has real part (dielectric constant) and imaginary part (dielectric loss). The real and imaginary values of permittivity are related to the constant n and k.

Real part , $\varepsilon' = n^2 - K^2 = 2.7325^2 - (8.6801 * 10^{-9})^2 = 7.4665$

Imaginary part, $\varepsilon'' = 2nk = 2 * 2.7325 * 8.6801 * 10^{-9} = 4.7437 * 10^{-8}$

Permittivity, $\varepsilon^* = \varepsilon' + i\,\varepsilon'' = 7.4665 + i\,4.7437 * 10^{-8}$

CHAPTER V

CONCLUSION AND RESULT

Absorption spectra can be used to determine the concentration of a solution of unknown concentration. Absorption data of a series of solutions of known concentrations creates an absorbance curve. Then, the unknown solution can be compared to this curve to determine the concentration. Linear fitting of Absorbance Vs Concentration was performed for zinc ferrite and dyes so that intercept and slopes are obtained. Photocatalytic degradation being an application we estimated the concentration of dye before and after exposure under sunlight. There is a reduction in peak absorbance which is an indication of a reduction in the concentration of dye, given by Beer–Lamberts' law. Methylene Blue shows photocatalytic degradation of concentration from 0.010043 to -0.018153 in a time interval of 120 minutes. Similarly, Methyl Orange shows a decrease in concentration from 0.07784 to 0.38734 in a time interval of 120 minutes. Zinc ferrite nanoparticles contribute to the formation of photogenerated electron-hole pair due to its low band gap facilitating photodegradation of the dye. This indicated that the mechanism could be attributed to the role of superoxide radicals in the photocatalytic degradation of the dye. Direct band gap and optical constants of zinc ferrite were computed.

Refractive Index	$n = 2.7325$
Band gap	$E_g = 2.05eV$
Extinction Coefficient	$k = 8.6801 * 10^{-9}$
Permittivity	$\varepsilon^* = 7.4665 + i\, 4.7437 * 10^{-8}$

CHAPTER VI

REFERENCE

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